

Autoxidation of Tetralin in Water catalysed by Cobalt(II)–Pyridine Complexes bound to Polymer Colloids

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Cobalt(II)–pyridine complexes bound to 60 nm diameter latex copolymers of styrene, divinylbenzene, and either acrylic or methacrylic acid catalyse autoxidation of tetralin in water faster than cobalt(II)–pyridine complexes in aqueous solution or cobalt(II) acetate in acetic acid.

Cobalt–pyridine (CoPy) complexes bound to copolymers of styrene and acrylic or methacrylic acid catalyse the autoxidation of 1,2,3,4-tetrahydronaphthalene (tetralin) dispersed in water [equation (1)]. Even though the solubility of tetralin in water, estimated to be less than 10^{-4} M (naphthalene, 1×10^{-4} M at 25 °C; tetralin 1.4×10^{-3} M at 150 °C),¹ oxidation of more than 60% of 0.06–0.13 M dispersed tetralin in the aqueous colloids occurs in 24 h at 50 °C at 1 atm pressure of dioxygen. The rate of tetralin oxidation with a colloidal CoPy catalyst is twice as fast as with aqueous CoPy and nine times as fast as with cobalt(II) acetate in acetic acid. The standard method of autoxidation of alkylaromatic hydrocarbons involves treatment with dioxygen in acetic acid with cobalt(II) as catalyst and HBr as promoter to yield 1,2,3,4-tetrahydro-1-naphthol (1-tetrol) and 3,4-dihydronaphthalen-1(2H)-one (1-tetralone) as the major products.^{2–4}

Copolymer latexes of styrene, acrylic acid (AA), or methacrylic acid (MA), and divinylbenzene were prepared by emulsion polymerization using sodium dodecyl sulphate as the surfactant and $K_2S_2O_8/NaHSO_3$ as a redox initiator.⁵ Cross-linking with divinylbenzene ensured that the polymer was insoluble during all subsequent experiments. The carboxylic acid groups were converted to Co^{II} salts *via* the potassium salt by addition of cobalt(II) acetate solution to the copolymer latex with agitation in an ultrasonic bath. The Co^{II} latexes specified in Table 1 were purified by ultrafiltration through a 0.1 µm cellulose acetate/nitrate membrane (Millipore) until the conductivity of the filtrate at 25 °C was constant at $40 \mu\Omega^{-1} \text{ cm}^{-1}$. An upper limit of 3×10^{-6} for the fraction of Co^{II} not bound to the latex was established by addition of 1,10-phenanthroline to the ultrafiltrate and u.v.–visible spectrophotometric analysis of the Co^{II} complex. By the same criterion, addition of 6 mol of pyridine per mol of Co^{II} to form the active catalysts did not extract cobalt ions from the latex. Autoxidations of tetralin are listed in Table 2 and illustrated in Figure 1.

A complete mechanism for the autoxidation of alkylaromatic hydrocarbons by cobalt(II) in acetic acid has not been established,⁶ although a complex rate law has been determined for tetralin.^{2,3} We decline to speculate here on the mechanism with colloidal CoPy catalysts, and are continuing study of the kinetics to gain a better understanding of the processes and to prepare still more active catalysts.

Table 1. Colloidal copolymers and catalysts.

| Catalyst | Copolymer ^a | CO ₂ H/ Co ^{II} | mg-atom Co/ g polymer | Wt. % solids | d/ nm ^b |
|----------|------------------------|--|-----------------------------|-----------------|-----------------------|
| LC-1 | 79:20 MA:1 | 18.6 | 0.11 | 2.1 | 58 |
| LC-2 | 79:20 MA:1 | 8.0 | 0.25 | 1.3 | 58 |
| LC-3 | 79:20 AA:1 | 17.4 | 0.12 | 2.0 | 62 |
| LC-4 | 23:76 AA:1 | 2.3 | 4.2 | 1.0 | 140 |

^a Mol % ratio of styrene : acrylic acid (AA) or methacrylic acid (MA); divinylbenzenes (55% technical grade) and ethylvinylbenzenes in the monomer mixture. ^b Number average particle diameter measured on transmission electron micrographs.

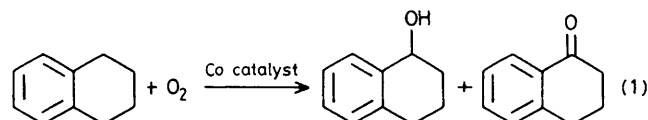


Table 2. Oxidation of tetralin using latex catalysts.^a

| Expt. | Catalyst ^b | Initial composition | | | Analysis, as mol% of initial tetralin | | | | |
|-------|-----------------------|----------------------|-------|-------------|---------------------------------------|-----------------------------------|------------------------------|-----------|--------------------|
| | | Co ^{II} /mM | Py/mM | Tetralin/mM | O ₂ consumed | Tetralin consumed ^c | Products formed ^c | | |
| | | | | | | | Tetrol | Tetralone | Other ^d |
| 1 | LC-1 | 0.66 | 4.0 | 61 | 69 | 65 | 22 | 43 | 3 |
| 2 | LC-1 ^e | 0.66 | 4.0 | 61 | 74 | 77 | 24 | 46 | 4 |
| 3 | LC-2 | 0.66 | 4.0 | 61 | 62 | 58 | 21 | 37 | 2 |
| 4 | LC-3 | 1.40 | 8.4 | 130 | 68 | 63 | 20 | 43 | 2 |
| 5 | LC-4 | 1.40 | 8.4 | 130 | 48 | 45 | 16 | 27 | 1 |
| 6 | LC-1 | 1.90 | 12.0 | 100 | 67 | 62 | 21 | 41 | 3 |
| 7 | CoPy ^f | 1.90 | 12.0 | 100 | 45 | 43 | 15 | 28 | 2 |
| 8 | CoAc ^g | 1.90 | — | 110 | 25 | 24 | 2.5 | 23 | 1 |

^a Reactions were carried out at 50 ± 0.1 °C for 24 h and an O₂ pressure of 720 mmHg (*ca.* 20 mmHg less than atmospheric pressure) with magnetic stirring of 30.0 ml of reaction mixture. Catalysts were equilibrated at 50 °C under oxygen prior to addition of tetralin. ^b Table 1.

^c From g.l.c. analysis of organic compounds extracted after coagulation of the latex catalyst with sodium chloride solution. ^d Unidentified product as weight % of initial tetralin. For detailed analysis of tetralin autoxidation products see A. Robertson and W. A. Waters, *J. Chem. Soc.*, 1948, 1574. ^e The mixture was agitated using a platform shaker having an amplitude of 2.5 cm and a frequency of *ca.* 1 s^{-1} .

^f Catalyst was soluble cobalt(II)–pyridine in water at pH 8. ^g Cobalt(II) acetate in acetic acid.

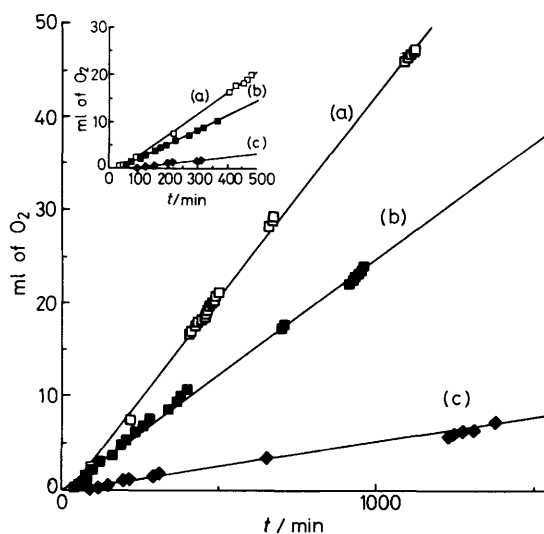


Figure 1. Oxygen consumption with time during autoxidation of tetralin catalysed by (a) LC-1, (b) aqueous CoPy, and (c) cobalt(II) in acetic acid. Inset shows induction periods.

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